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COMPARISON OF WOOD CELLULOSE AND COTTON CELLULOSE

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COMPARISON OF WOOD CELLULOSE AND COTTON CELLULOSE[1]

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Summary

Data recorded in this paper show that the wood cellulose most nearly corresponding to cotton, taking purified linters as a standard, is obtained by recooking "easy bleaching" sulfite pulp with soda and bleaching with 2 percent bleach. The significant differences are found in the amounts of furfural-yielding constituents present and in the gamma-cellulose contained in this pulp, but which is not found in the linters. This sample, however, represents the lowest yield on the basis of the original wood.

The recooked, raw cooked sulfite pulp (232 LR) bleached with 3 percent bleach does not differ so markedly from the above sample and represents a 6 percent higher yield on the basis of the original wood. Esterification tests might show this to be a suitable form of raw material, assuming that similarity to cotton cellulose is a prerequisite for wood cellulose for this purpose.

Since the data show that bleaching is a very efficient method of removing the noncellulose material, it is probable that the yield of cellulose suitable for the manufacture of esters could be materially increased by giving a light or raw cooked stock a bleaching treatment prior to recooking with soda.

Alkaline cooking produces a larger amount of beta-cellulose than acid cooking, the amount increasing with the severity of the cooking conditions. From a chemical standpoint, pulps produced by alkali are less similar to cotton than those produced by acid cooking or by acid and alkaline cooking. On this basis the former appears to be less suitable for esterification.

On the basis of the data given, cellulose from wood and cellulose from cotton do not represent identical chemical aggregates, and the

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R1036

same is true of wood celluloses obtained by acid cooking and by alkaline cooking. The practice of checking wood cellulose according to the specifications for cotton is, therefore, a questionable procedure.

Introductory

It is customary in determining the suitability of wood cellulose, to be employed as a substitute for cotton cellulose in the manufacture of cellulose esters, to refer the former to specifications ordinarily applied to cotton. This practice is perhaps due more to lack of data regarding the celluloses than to lack of appreciation of the possible differences in the nature of these chemical aggregates. It is, of course, possible to obtain a cellulose from wood by suitable means of degradation that approximates cotton cellulose, but available information indicates that cellulose from wood can not be made identical with cellulose from cotton. To obtain a product that even approximates cotton cellulose entails a loss so great that it renders the process uneconomical.

In connection with a study of the preparation of wood cellulose suitable for the manufacture of cellulose esters comparisons were made of wood and cotton celluloses varying in purity from the original raw materials to severely cooked and highly bleached samples, for the purpose. (1) of following the chemical changes which occur in wood pulps on successive cooking and bleaching treatments in order to determine whether the conditions in these treatments could be changed so as to increase the yield of suitably purified cellulose and (2) to determine so far as possible the points of similarity or difference of cellulose from wood and that from cotton. Data of this nature should be of value not only in the manufacture of cellulose esters, but also in all allied industries involving the chemical utilization of cellulose and also in the pulp and paper industry.

Experimental[2]

Since even "normal" or cotton cellulose is still an uncertain chemical entity the method of attack in making these comparisons consisted in determining the constants usually stipulated in specifications for cotton[3] and also certain constants which have been employed in the analysis of the ligno-celluloses.[4] The determinations made will be

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[2] Acknowledgment is made to Messrs. M. W. Bray and J. A. Staidl for assistance in securing the data given in this paper.

[3] Weaver "Military Explosives" (1912) 188; Marshall "Explosives" (1917) 696; Paper (1919) V.23, No.23.

[4] Jour. of Ind. & Engin. Chem. 9 (1917) 556; Cross and Bevan "Paper-making" (1916) 93.

briefly outlined and the experimental data given after which the results will be discussed and such comments made on methods as seems necessary.

Moisture was determined by drying at 105° C.; waxes, fats, and resins were found by extraction with ether for 4 or 5 hours; solubilities in 1 percent alkali and in hot and cold water were obtained by treatment with those reagents for 1, 3, and 48 hours, respectively. Pentosans and methyl pentosans were determined by distilling the material under investigation with 12 percent hydrochloric acid (Sp.gr. 1.06), treating the furfural contained in the distillate with phloroglucinol, weighing the resulting mixed phloroglucides, and weighing again after the extraction of methyl furfural phloroglucide by means of alcohol. Cellulose determinations were made by a modification of the method of Cross and Bevan and involve alternate treatment with chlorine gas and a 2 percent solution of sodium sulphite to a point where no color results with the sulphite solution after treatment with chlorine. Acetic acid by hydrolysis was found by boiling for 3 hours with 2.5 percent sulphuric acid, distilling the acid extract under a pressure of 40 to 50 mm. and titrating the resulting distillate with standard alkali. Methoxy groups were determined by distilling with hydriodic acid according to the Zeisel method.

Lignin or the noncellulose content was obtained by a modification of the method of Ost and Wilksening[5] employed in the hydrolysis of cellulose. Four grams of the pulp was extracted with ether and treated with 10 times its weight of 72 percent sulphuric acid and the hydrolysis allowed to proceed for 16 hours at room temperature. The solution was then diluted to 3 percent and boiled under a reflux condenser for 2 hours. This caused a coagulation of the suspended material and the residue was then filtered on an alundum crucible and dried and weighed.

Solubility in 7.14 percent sodium hydroxide (or 10 percent KOH), which is regarded as a measure of the degree of bleaching, was determined by treatment of two grams of oven-dry pulp with 100 cc. of alkali at 100° C. A flask provided with a reflux condenser and containing the mixture was heated in a salt bath for exactly 3 hours. The mixture was then acidified with acetic acid and the residue filtered off, dried and weighed.

The "copper number"[6] is also regarded as a measure of the degree of bleaching. This value was obtained by treating 2 grams of

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[5] Cross and Bevan "Researches on Cellulose," III (1905-10) 39.

[6] Schwalbe, "Chemie der Cellulose" (1911) 625.

pulp with 50 cc. of Fehling solution and boiling under a reflux condenser on a hot plate for exactly 15 minutes. The residue was then filtered off on an alundum crucible and washed free from alkali. The copper oxide was dissolved in nitric acid (10.7 percent) and the amount of copper determined by titration with thiosulphate solution under standard conditions.[1]

The cellulose isolated by the chlorination method was examined for alpha-, beta-, and gamma-cellulose by treatment with caustic soda solution of mercerizing strength (17.5 percent NaOH).[2] Weighed amounts (approximately 2 grams) of cellulose were treated with a volume of alkali amounting in cc. to 10 times the weight of the cellulose and allowed to stand for exactly 30 minutes at room temperature with frequent agitation. The alkali was then diluted with an equivalent volume of water and the undissolved residue filtered on an alundum crucible. The alpha-cellulose which remains on the crucible is washed free from alkali with the aid of dilute acetic acid, dried and weighed. The filtrate is acidified with acetic acid and heated on a water bath to coagulate the beta-cellulose which is then filtered off, washed thoroughly, dried and weighed. The portion of the cellulose permanently dissolved is gamma-cellulose.

Materials Investigated

The cotton samples examined consisted of (1) raw linters containing about 20 percent of hulls, (2) nonmedicated commercial absorbent cotton, (3) munition linters prepared by cooking raw linters with 20 percent of their weight of sodium hydroxide at a concentration of 2.6 percent, and (4) pulped linters prepared by cooking raw linters with a lime-soda-ash liquor containing approximately 8.8 pounds of caustic soda to 100 pounds of raw linters.

The wood cellulose samples analyzed were prepared by Messrs. S. D. Wells and V. P. Edwardes of the Section of Pulp and Paper of the Laboratory by varying the usual cooking conditions somewhat. White spruce (Picea canadensis) was the raw material used in all the cooks. Bleached samples were prepared from each of the pulps by subjecting them to the varying amounts of bleaching powder indicated in the tables. The bleaching was carried out at a temperature not exceeding 38° C. and allowed to continue to exhaustion of the bleaching solution. A summary of the yields of bleached and unbleached pulps is given in Table 1.

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[1] Journal American Chemical Society, 34 (1912) 422.

[2] Cross and Bevan, "Researches on Cellulose," III (1905-10) 23; Cross and Bevan, "Paper-making," (1916) 97; Schwalbe, "Chemie der Cellulose" (1911) 637.

The analytical data obtained on these samples are given in Table 2. In the case of the sulphite pulps the letters "L" and "W" indicate light or raw cooked and well or normal cooked pulps, respectively. "R" indicates the pulp has been recooked with a weak (1 percent) caustic soda liquor. In the soda and sulphate runs "L" indicates a light or normal cooked pulp while "W" indicates a well or severely cooked pulp.

The samples were air dried in the form of paper and the material prepared for analysis by running it through a shredder which gave a fluffy product with the individual fibers more or less separated.

Discussion of Results

Moisture

These values were determined for the purpose of obtaining a basis on which to calculate the results of the other determinations. The samples were exposed long enough to be air dried at 68° F. in an atmosphere having a relative humidity of approximately 25 percent.

Wood cellulose obtained by acid cooking is more hygroscopic than that from alkaline treatment although the reverse has been observed for cotton cellulose.[9] The unbleached sulphite pulps are more hygroscopic than raw linters and absorbent cotton while the alkaline pulps, excepting the light cooked sulphate are less hygroscopic. Bleaching decreases the hygroscopicity of the sulphite pulps, but increases the affinity for water of those pulps that have been subjected to alkaline treatment.

Ash

All celluloses retain a certain amount of the mineral constituents contained in the original raw material irrespective of the method employed in their isolation. Schorger[4] found cellulose from spruce wood to contain an average of 0.30 percent ash. Purified cotton yields an ash ranging from 0.10 to 0.50 percent while raw cotton contains 1 percent or more of mineral constituents.[10] The ash values in the wood celluloses examined, while fairly uniform for each series, are high compared to spruce wood on the one hand and to purified cotton on the other. The high values are undoubtedly due to insufficient washing of the pulps and to the tendency of cellulose to adsorb mineral salts.

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[9] Schwalbe "Chemie der Cellulose" (1911) 13.

[10] Schwalbe "Chemie der Cellulose" (1911) 34.

TABLE I—YIELDS OF PULP

(Results expressed in per cents, based on oven-dry weight of wood)

Unbleached Pulps Sample No.	Cook No.	Nature of Cook	Yields Unbleached Pulps	Yields—Bleached Pulps									
				Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield	Bleaching Powder	Yield
221 L	7	Sulfite	61.3	..	..	..	..	..	..	25	57.3	50	53.6
231 LR	7	Recook	39.4	3.0	39.2	..	..	5	38.8	8	38.7	12	39.2
221 W	8	Sulfite	47.3	2.5	47.9	6	45.6	12	46.2	20	45.5	30	46.4
231 WR	8	Recook	33.3	2	32.7	..	..	5	32.4	7	32.3	12	32.0
201 W	2	Soda	33.8	..	..	7	32.8	10	31.8	15	32.5	..	..
201 L	3	Soda	42.8	..	..	12	41.9	..	..	20	40.7	..	..
211 W	4	Sulfate	39.0	..	..	6	38.7	15	39.2	..	..	..	..
211 L	5	Sulfate	48.2	..	..	10	47.6	..	..	25	46.2	..	..

(3)

TABLE II

Sample Number or Designation	Bleaching Powder (35 Per cent Available Cl), Per cent	Moisture	Ash	Cold-Water-Soluble 48 Hrs.	Hot-Water-Soluble 3 Hrs.	Alkali-Soluble 1 Per cent NaOH 1 Hr.	Acetic Acid by Hydrolysis	Ether Extract	Pentosan	Methylpentosan	Furfural	Alkali-Soluble 7.14 Per cent NaOH 3 Hrs.	Methoxy Groups (CH_3O)	Cellulose	In Cellulose: α-Cellulose	In Cellulose: β-Cellulose	In Cellulose: γ-Cellulose	In Cellulose: Pentosan	In Cellulose: Methylpentosan	Furfuroids	Lignin (Noncellulose)	G. Cu per 100 G. of Sample
Spruce sulfite pulp, air-dried, results expressed in per cent, calculated on oven-dry (105° C.) weight of pulp[1]																						
Spruce wood	0.00	..	0.31	1.12	2.14	11.57	1.59	1.36	10.39	3.55	..	..	5.30	61.85	..	..	..	9.63	0.72	..	..	..
221 L	0.00	7.99	1.72	2.54	2.76	9.77	0.24	2.10	5.43	3.03	4.15	26.46	2.26	82.72	83.50	0.31	16.19	6.97	1.48	4.43	11.92	2.18
223 L	25.00	6.44	1.36	1.53	3.98	18.14	0.03	0.63	7.07	1.75	4.63	26.93	1.58	87.13	83.70	2.32	13.98	7.07	1.04	4.29	4.08	3.50
224 L	50.00	6.19	1.21	2.15	3.57	16.21	0.02	0.66	6.67	1.63	4.32	26.36	0.72	93.18	83.25	3.39	13.36	6.06	1.11	3.75	0.46	3.04
231 LR	0.00	4.86	1.41	0.30	0.00	1.52	0.05	0.55	4.55	1.14	2.93	5.84	0.58	96.75	85.95	1.71	12.54	4.10	0.84	2.51	2.75	0.95
232 LR	3.00	4.80	1.57	0.68	0.58	2.97	0.08	0.97	3.95	1.19	2.59	6.70	0.35	94.78	94.45	2.46	3.09	4.28	0.95	2.65	3.01	1.12
233 LR	5.00	4.66	1.73	1.21	1.68	3.89	0.11	1.04	3.91	1.21	2.60	8.72	..	94.29	94.49	2.16	3.35	5.09	1.68	3.36	2.82	1.36
234 LR	8.00	5.32	1.78	0.83	1.13	4.62	0.08	0.77	4.17	1.35	2.76	12.41	..	95.60	92.15	3.51	4.34	4.17	2.02	2.93	1.95	1.84
235 LR	12.00	4.94	1.91	1.51	2.41	8.36	0.09	1.57	4.49	1.18	2.96	21.26	..	93.30	89.05	5.97	4.98	4.29	1.26	2.75	1.15	2.53
221 W	0.00	5.59	0.49	0.84	1.24	5.67	0.09	1.45	4.94	1.64	3.31	19.89	1.06	94.95	87.60	2.98	9.42	5.14	1.55	3.39	1.99	2.42
223 W	6.00	5.03	0.78	0.39	0.87	12.35	0.12	1.20	5.74	1.06	3.60	19.89	0.65	96.33	88.25	2.53	9.22	5.63	2.43	3.92	1.14	2.62
224 W	12.00	5.11	0.58	0.30	0.76	11.74	0.20	1.13	5.90	1.16	3.72	23.70	0.55	97.01	87.12	3.91	8.97	4.78	1.76	3.22	0.66	2.47
225 W	20.00	5.17	0.91	1.22	1.54	18.27	0.32	0.76	5.96	1.25	3.76	32.76	0.53	98.89	88.25	7.93	8.82	5.53	1.98	3.73	0.13	3.83
231 WR	0.00	4.41	0.75	0.29	0.12	0.14	0.02	0.73	2.61	1.04	1.76	3.63	0.21	98.17	90.20	2.49	3.00	2.34	0.88	1.51	0.96	1.12
232 WR	2.00	4.61	0.78	0.23	0.51	2.06	0.06	0.64	2.48	0.62	1.54	5.31	0.37	98.10	95.10	1.90	7.31	2.35	1.55	1.70	1.04	1.20
233 WR	5.00	5.18	1.01	0.00	0.28	4.17	0.00	0.72	2.51	0.69	1.60	12.81	..	98.07	93.80	3.84	2.86	2.36	1.17	1.83	0.59	1.93
234 WR	7.00	5.26	0.87	0.41	0.54	7.03	..	0.61	2.65	0.75	1.69	20.02	..	97.68	90.00	7.73	2.27	2.22	1.09	1.50	0.49	2.69
235 WR	12.00	5.34	1.00	0.93	1.76	16.38	..	0.53	3.35	0.80	2.10	36.87	..	95.61	74.80	21.20	4.00	2.33	1.19	1.59	0.44	6.92
Cotton, air-dried, results calculated on oven-dry (105° C.) weight of material analyzed																						
Raw linters	0.00	4.13	1.57	2.00	2.27	7.67	0.16	0.50	1.58	0.52	0.98	12.22	0.36	89.75	83.19	1.87	14.95	0.46	0.32	0.20	8.15	4.55
Absorbent cotton	0.00	4.34	0.11	0.00	0.00	1.75	0.04	0.31	0.58	0.48	0.30	6.20	0.39	98.93	87.60	12.20	0.12	0.50	0.85	0.16	0.36	1.13
Purified linters[3]	2–3	2.67	0.52	0.33	0.23	1.52	0.10	0.24	1.11	0.46	0.63	3.72	0.37	99.32	97.40	2.60	0.00	0.45	0.77	0.30	1.35	0.87
Pulped linters[3]	6–8	2.25	0.64	0.50	0.38	6.46	0.04	0.28	1.97	0.70	1.27	16.67	0.31	97.90	88.30	11.7	0.00	1.31	1.03	0.88	0.12	2.57
Spruce soda and sulfate pulps, air-dried, results calculated on oven-dry (105° C.) weight of pulp																						
201 L-Soda	0	3.91	1.12	0.71	0.26	2.81	0.07	0.49	7.77	1.14	4.82	5.93	0.89	93.17	85.66	7.81	6.53	7.31	1.52	4.59	4.03	1 59
202 L-Soda	12	6.26	0.92	0.58	1.07	4.93	0.06	1.10	8.24	1.18	5.09	12.03	0.57	94.26	60.57	34.19	5.24	7.45	1.33	4.63	5.86	1.76
203 L-Soda	20	5.79	0.90	1.27	1.21	6.92	0.04	0.71	8.20	1.35	5.12	17.06	0.32	94.77	53.01	35.07	11.92	6.80	1.50	4.32	4.55	2.40
201 W-Soda	0	3.48	0.90	1.27	0.62	2.46	0.06	0.41	3.82	1 25	2.54	5.89	0.47	96.20	80.30	13.27	6.43	3.42	1.54	2.33	2.11	1.09
203 W-Soda	7	4.94	0.91	0.51	0.08	3.40	0.06	0.52	3.98	1.66	2.76	7.14	0.26	97.16	55.93	34.22	9.85	3.87	1.88	2.71	2.66	1.66
205 W-Soda	15	5.66	1.22	0.45	0.18	9.81	0.04	0.76	4.09	0.63	2.54	22.15	0.29	97.05	51.50	37.80	10.70	3.41	1.92	2.48	2.22	3.61
211 L-Sulfate	0	4.89	1.16	1.25	0.40	2.62	0.10	1.65	10.04	0.92	6.09	8.61	0.68	94.56	84.20	6.31	9.49	9.96	1.29	6.10	3.39	1.38
212 L-Sulfate	10	6.04	1.27	0.59	0.00	3.61	0.04	1.42	10.07	0.64	6.05	11.64	0.26	94.00	64.70	23.98	11.32	8.30	1.70	5.26	5.53	1.67
213 L-Sulfate	25	5.97	1.40	1.23	0.91	14.02	0.04	1.10	9.90	0.85	6.00	31.04	0.25	94.56	56.87	31.55	11.58	8.46	1.46	5.27	4.04	3.93
211 W-Sulfate	0	3.64	1.01	1.23	0.82	2.18	0.06	0.63	6.05	1.07	3.79	5.51	..	96.17	81.80	10.31	8.07	5.81	1.62	3.85	1.88	1.46
213 W-Sulfate	6	5.74	0.83	0.00	0.00	2.28	0.03	0.89	7.67	1.35	4.51	7.10	0.24	95.68	72.20	18.72	9.08	6.95	1.01	4.28	3.43	1.58
214 W-Sulfate	15	5.49	1.21	0.00	0.00	8.51	0.04	0.93	7.17	1.62	4.22	20.47	0.18	95.40	62.95	26.90	10.15	6.20	0.97	3.84	2.64	2.98

[1] The values given except those in the column headed "In Cellulose," are averages of two closely agreeing duplicates.

[2] Values obtained by Schorger, THIS JOURNAL, 9 (1917), 556.

[3] The low moisture content of these two samples is due to their having been dried over a steam-heated radiator.

Water-Soluble Content

Cellulose is generally regarded as insoluble in water.[11] While the water soluble content of the samples analyzed may be accounted for in part by soluble salts retained from previous treatments many of the samples show appreciable amounts of water soluble material which can not be accounted for in this way. The wood celluloses isolated appear to contain more water soluble material than the treated cotton cellulose. The sulphite pulps are more soluble in hot than in cold water under the conditions of these experiments while the reverse is true of the pulps from alkaline treatment. Bleaching increases the solubility of the sulphite pulps, but tends to decrease the solubility of the soda and sulphate pulps. Cross and Bevan[12] have recently shown that cotton cellulose is changed both qualitatively and quantitatively by contact with water.

Alkali-Soluble Content

The solubility test in 7.14 percent sodium hydroxide is in reality an alkali-acid solubility test, since the alkaline solution is acidified before filtering. This almost invariably results in the precipitation of some material (probably analogous to beta-cellulose) which would otherwise remain in solution. Notwithstanding this difference in procedure, the values for solubility in 1 percent alkali and 7.14 percent alkali parallel each other in practically all cases.

In general, increased solubility in alkali results from increased bleaching, but notable exceptions to this are found in the case of the light or raw cooked (221L series) sulphite pulp. The results obtained in the light cooked series where no increase in solubility occurs on bleaching are due to two compensating changes which take place. As indicated by the lignin values, bleaching removes the noncellulose material, which is more or less soluble in alkali, on the one hand and produces alkali soluble constituents from the residual cellulose on the other. The effect is a practically constant percentage of alkali soluble material with 7.14 percent sodium hydroxide. With 1 percent alkali the two changes do not compensate so closely, but their effect is quite apparent.

Several of the recooked samples which have been lightly bleached, together with both of the soda pulps and the well cooked sulphate pulp approach munition linters and absorbent cotton in their degree of solubility in alkali. In general, however, the wood celluloses are more soluble than cotton cellulose which has been subjected to corresponding treatment.

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[11] Schwalbe "Chemie der Cellulose" (1911) 19.

[12] "Cellulose" (1918) 311.

The solubility in 7.14 percent sodium hydroxide is apparently due to the presence of lignin, furfural-yielding constituents and gamma-cellulose in the pulp and also to the conversion of some of the more resistant celluloses into soluble form during the 3 hours boiling with the alkali in the test. Evidence for this is given in Table 3 where the solubility in alkali on the one hand is compared with the beta- and gamma-cellulose and loss on chlorination on the other. In the alkaline pulps the conversion of insoluble to soluble cellulose has apparently reached its limit in the original cook.

Table 3.

Sample number	7.14 percent NaOH soluble	Beta- and gamma-cellulose*	Loss on chlorination
	Percent	Percent	Percent
221L	26.46	17.18	17.18
223L	26.93	13.97	12.87
224L	26.36	15.61	6.72
221W	19.89	11.78	5.05
223W	19.89	11.31	3.67
224W	23.70	12.49	2.99
225W	32.76	16.06	4.11
231WR	3.63	9.85	1.87
232WR	5.31	4.81	1.90
233WR	12.81	6.57	1.93
234WR	20.02	9.00	2.32
235WR	36.87	24.09	4.39
Munition linters	3.72	2.58	.68
201L-Soda	5.93	13.36	6.83
201W-Soda	5.89	18.95	4.80
211L-Sulphate	8.61	14.94	5.44
211W-Sulphate	5.51	17.68	3.83

*Calculated on the basis of the original pulp.

If time and temperature of treatment and strength of alkali were the same in the alkali solubility determination and in the determination of alpha-, beta-, and gamma-cellulose the sum of columns 2 and 3 would more nearly approximate column 1. That the 7.14 percent solubility figures are in the main greater than this sum in the case of the sulphite pulps, especially those which have not been redigested, indicates that

this solubility test is too severe a test for these pulps as considerable of what is determined as alpha-cellulose is dissolved during the test.

Acetic Acid by Hydrolysis

Spruce wood yields on hydrolysis with dilute sulphuric acid 1.59 percent of fatty acids consisting almost entirely of acetic acid. The data show the acetyl groups producing this acid to be removed both by acid and alkaline cooking. Acetic acid residues, if present in the wood, are not resolved by subsequent cooking or bleaching into a condition in which they yield acetic acid on further hydrolysis with dilute sulphuric acid. The recooked sulphite pulps and also the soda and sulphate pulps correspond with cotton in yielding practically no acetic acid by hydrolysis.

Ether Extract

This extract contains the waxes, fats, resins, etc. not removed from the pulps by cooking. Spruce wood yields an extract of 1.36, while subjecting this wood to mild acid cooking tends to concentrate the extractive material in the pulp as is shown in Sample 221L. Strong bleaching, however, tends to reduce the amount of extractives in the sulphite pulps, but does not cause an elimination of them beyond a certain point as indicated in the well cooked series. The cottons yield smaller amounts of extractive materials than the woods. Soda cooking is slightly more efficient in removing these materials than sulphite or sulphate cooking. Subsequent bleaching of the soda and sulphate pulps, in contrast with the sulphite pulps, does not remove any of the residual extractives. In fact, the percentage of ether soluble constituents appears to be slightly increased by the action of bleaching powder on the alkaline pulps. The two soda cooks are nearest the maximum specification of 0.4 percent of extractive matter for cotton, but none of the samples of pulp meet this requirement.

Pentosan, Methyl Pentosan, and Furfuroids

The furfural and methyl furfural-yielding constituents of wood are usually calculated in terms of pentosan and methyl pentosan and this procedure was followed in tabulating the present results. Since the extraction of methyl furfural-phloroglucide with alcohol is not entirely satisfactory the results are also calculated in terms of furfural which eliminates the effect of this extraction in the data recorded under the heading of "Furfuroids" and which gives values more comparable than the values under the other two headings. In general, however, the values in all three columns parallel each other rather closely.

The chief source of furfural in woods are the pentosans although the lignin also contains furfural-yielding constituents. In pulps there may be hydrocellulose and oxycellulose present which also yields furfural. Since the yield of furfural from each series of pulps is constant or nearly so the indication is that very little hydrocellulose or oxycellulose is formed during bleaching. This seems to show that the solubility of the pulps in alkali, which increases rapidly with increased bleaching and which is usually attributed to the above modifications, is due to some other change in the cellulose.

The pulps contain larger percentages of pentosan and methyl pentosan than the cottons. To what extent this makes them less suitable than cotton for esterification has not been fully determined although it is commonly regarded that, in cellulose for nitration, the presence of lower carbohydrate bodies leads to a less stable nitration product.

Methoxy Content

Methoxy groups are characteristic of the lignified celluloses. They are contained chiefly in the lignin and are, therefore, largely removed by cooking and by bleaching. The absence of methoxy groups is regarded as an indication of a very pure form of cellulose. The bleached soda pulps and the recooked sulphite pulps compare very favorably with the cottons which are shown to contain very small amounts of methoxy. Benedikt and Bramberger[13] found no methyl groups in cotton, but small amounts in sulphite cellulose.

Cellulose

The yields of cellulose from the pulps by the chlorination method more nearly approach those from cotton in the case of the recooked normal cooked sulphite pulp and the well cooked soda and sulphate pulps. There is, however, considerable difference in the nature of these celluloses when the alpha-, beta-, and gamma-celluloses and furfural-yielding constituents in them are considered. The gamma-cellulose for each series of bleached pulps is fairly constant, but is less than that for the unbleached pulps of the same series in the case of the sulphite pulps and greater in the case of the soda and sulphate pulps. All the wood celluloses contain more gamma-cellulose than the purified cotton samples. In the manufacture of nitrocellulose gamma-cellulose is said to be lost during nitration[14] and, therefore, reduces the yield of nitrocellulose obtained.

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[13] Monatshefte 11, 260-67.

[14] Jour. of Industrial & Engin. Chem., 12 (1920) 382.

Pulps obtained by the alkaline cooks contain a higher percentage of beta-cellulose than those obtained by the acid cooks. Mild bleaching has little effect, but heavy bleaching converts alpha-into beta-cellulose. Upon nitration beta-cellulose is said to give a less stable product, but the evidence on this point is not conclusive.

Furfuroids as pointed out by Cross and Bevan[15] appear to be normal constituents of cellulose isolated from wood. This differentiates wood cellulose from cotton cellulose although the data show the latter to contain small amounts of furfural-yielding constituents.

The sample which is the nearest approach to the purest cotton sample (munition linters) from the standpoint of the nature and yield of cellulose is the recooked normal cooked sulphite pulp (232WR) bleached with 2 percent bleach.

Lignin

The term lignin is rather indefinite and is commonly applied to that portion of wood which is not cellulose. In this paper lignin is defined as the residue insoluble in 72 percent sulphuric under the conditions already outlined. The values given are not corrected for ash since the ash content for each series of samples is practically constant.

A stronger concentration of acid is sometimes employed in this determination. However, we obtained higher values using 95 percent sulphuric acid as indicated by the following figures:

Sample number	72 percent sulphuric acid: Percent	Mean	95 percent sulphuric acid: Percent	Mean
231 WR	1.05		1.65	
	.88	0.96	1.65	1.65

The procedure in making the determinations with 95 percent sulphuric acid was to treat the sample for 5 minutes with ten times its weight in cc. of acid. The reaction mixture was then diluted to twenty times its volume and boiled under a reflex condenser for 4 hours. The high values obtained are probably due to a certain amount of charring of the cellulose.[16]

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[15] "Cellulose" (1903) 83.

[16] Ztschr Physiol. Chem. (1882) 83 (7) 913.

Soft woods like spruce contain approximately 25 to 30 percent lignin, which as shown by the data is removed to a greater or less degree in the pulping process, depending upon the severity of cooking conditions and the nature of the process employed. The effect of bleaching in removing lignin from sulphite pulp is well indicated in each of the series of bleached samples, but particularly in the case of the raw cooked sulphite samples (221L series). On the other hand the inability of bleaching to remove the lignin from alkaline cooked pulp is well illustrated in the soda and sulphate samples. Bleaching appears to increase rather than decrease the amount of material insoluble in sulphuric acid. The well cooked sulphite pulps give values that agree well with those for cotton, but the pulps obtained by alkaline cooking run rather high in lignin.

Copper Number

The copper number was proposed by Schwalbe as a means of measuring the degree of bleaching of cellulosic materials and a detailed method of procedure was worked out in his laboratory for making the determination. The simpler method employed in this investigation, as already outlined, gives comparable results and is less tedious than the original method. Blank runs on Fehling's solution gave an average value of 0.38, which was assumed to be constant and the values were not corrected for it.

The values obtained increase with increasing amounts of bleach employed, but the unbleached samples also yield values of nearly the same magnitude as the mildly bleached pulps showing that products other than those produced in bleaching also reduce Fehling's solution. Bancroft[17] concluded that the reducing action on Fehling's solution is probably not characteristic of oxycellulose, to which it is in part attributed, but to decomposition products of the cellulose.

The differences in the copper number with increased bleaching are not so pronounced as the corresponding differences in the alkali solubility. The latter constant appears, therefore, to be more suitable as a means of determining the degree of bleaching than the copper number. The usual specification of a copper number not to exceed 1.0 would exclude all of the pulps except 231LR.

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[17] Jour. Phys. Chem. 19 (1915) 159.